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<b>(54) Title:</b> PROTECTION OF ALUMINUM PRODUCTION CELL COMPONENTS  <b>(57) Abstract</b>  Carbon-containing components, in particular sidewalls, of cells for the production of aluminum by the electrolysis of alumina dissolved in a cryolite-based molten electrolyte are protected from attack by liquid and/or gaseous components of the electrolyte, by a treatment composition which consists essentially of a solution of one or more non-colloidal phosphates of aluminum. The treatment composition may alternatively consist essentially of one or more non-colloidal phosphates of aluminum and one or more colloidal carriers.		

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## PROTECTION OF ALUMINUM PRODUCTION CELL COMPONENTS

### TECHNICAL FIELD

The invention relates to methods and compositions for treating carbonaceous components of aluminum production cells (particularly cell sidewalls as defined herein), and the treated components. Aluminum production cells utilizing the components produced by the methods herein are also included within the scope of the present invention.

### BACKGROUND ART

Aluminum is produced conventionally by the electrolysis of alumina dissolved in cryolite-based molten electrolytes at a temperature up to about 950°C (the Hall-Héroult process). A Hall-Héroult reduction cell typically comprises a cell bottom and corresponding sidewalls, said cell being made from a steel shell and having an insulating lining of refractory material (the term "sidewall" as used herein is intended to encompass those carbonaceous portions of aluminum production cells which are traditionally understood to be sidewalls, which are *not* in continuous, uninterrupted contact with the cryolite and/or the product aluminum). The refractory material, in turn, has a lining of carbon which contacts the molten constituents. Conductor bars connected to the negative pole of a direct current source are embedded in the carbon cathode substrate which forms the cell bottom floor. The cathode substrate is typically an anthracite-based carbon lining made of prebaked cathode blocks or graphite blocks which have been joined with a ramming mixture of anthracite, coke, and coal tar or with a resin. A pool of molten aluminum overlying the cathode blocks acts as the active cathode.

In Hall-Héroult cells, the carbon lining or cathode block material has a useful life of only three to eight years (even less under adverse conditions). The deterioration of the

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cathode bottom is due to erosion and penetration of electrolyte and liquid aluminum, as well as the intercalation of sodium species, which penetrate into the carbon and cause swelling and deformation of the cathode carbon blocks and ramming mix and even of the sidewalls. In addition, the penetration of air, sodium species or other components of cryolite leads to the formation of toxic compounds, including cyanides. In fact, problems associated with the penetration of sodium species into the carbon cathode bottom have been extensively discussed in the literature. This intercalation by sodium species leads to swelling of the carbon cathodes (particularly damaging during cell startup), displacement of the carbon blocks, and the production of large quantities of toxic compounds. The intercalation by sodium species also leads to increased oxidation of the carbon cathodes, which in turn results in a reduced life for the cell. Cell sidewalls are also susceptible to oxidation damage, since much of the sidewall is exposed to air. In the presence of sodium ions, the rate of oxidation of the sidewalls is increased.

For many years, despite extensive efforts and the potential advantages of having cell sidewalls which have surfaces of titanium diboride and other RHM materials, these materials were not commercially accepted by the aluminum industry.

While it is known that treatment by phosphates of aluminum protect against oxidation of carbonaceous substrates (see, for example, U. S. Patent No. 2685,539 which discloses the use of an aqueous solution of an aluminum phosphate compound for reducing oxidation of a carbonaceous substrate, the concentration of said solution being around 25%, wherein the molar ratio of  $\text{Al}_2\text{O}_3$  to  $\text{P}_2\text{O}_5$  is preferably between 0.4:1 and 0.6:1 and wherein the weight percentage of the phosphate compound is preferred to be between 1 and 10% by total weight of the carbonaceous substrate), the use of phosphates has been strongly discouraged in connection with aluminum production cell environments. This is because, it is known that phosphates cause contamination of the product aluminum and of the cryolite. Phosphorus can only be tolerated in the cryolite at a level of 5-10 ppm. At levels of 100 ppm phosphorus decreases the cell efficiency by about 0.9%. Therefore, the use of phosphates to prevent oxidation of cell sidewalls or other components is fraught with the risk of contaminating the cryolite and hence the product aluminum. Despite this strong *teaching away* in the prior art, the present

invention sets out to devise a method of utilizing phosphates without detrimentally contaminating the cryolite and/or the product aluminum. The prior art had attempted to solve the problem of oxidation of sidewalls primarily by using silicon carbide bricks and/or by using micropyrethically synthesized carbonaceous sidewalls. As explained below, high cost and an unexplained mechanism of selective disintegration has plagued the silicon carbide based sidewalls, whereas high cost has thus far prevented widespread acceptance of the micropyrethically synthesized carbonaceous sidewalls.

In devising a cost-effective method of preventing oxidation of aluminum cell components, particularly cell sidewalls, the present invention has taken into account the unexpected "natural" protection offered by the frozen or solidified cryolite "ledge". Thus, it was determined that during *normal* cell operation this cryolite ledge prevents possible contaminants like phosphates from entering the molten cryolite and also simultaneously prevents attack of the cell sidewall by the cryolite and hence reduces sodium penetration of the sidewall.

Despite this "natural" protection, there are certain situations during which contamination by the phosphates of the cryolite remains possible. Thus, the top part of the frozen cryolite crust is deliberately broken whenever it is necessary to feed alumina to the cell, during which time oxidizing gases may reach the cell sidewalls making the sidewall susceptible to oxidation because of the sodium attack. Also, the outside (toward the shell) portion of the sidewall is susceptible to oxidation due to oxidizing gases going through the passage around the conductor bar. Finally, the frozen cryolite ledge is unstable, being dependent on the thermal balances extant in the cell and may fail at certain points due to over insulation or due to the anode effect. In such situations, the sidewall is susceptible to sodium attack. Quite surprisingly, the invention has established that the protective phosphate based treatment methods of the present invention also prevent sodium and cryolite attack and concomitant swelling and oxidation of the sidewall.

### SUMMARY OF THE INVENTION

While not exclusive, the following describes some of the important features and objectives of the present invention:

It is an object of the present invention to provide a method for treating aluminum production cell components including sidewalls, to protect the components from corrosive attack by liquids and gases present within and outside the cells. The methods of the present invention are particularly useful for protection of sidewalls of such cells from the attack of sodium, cryolite and air in order to prevent intercalation of sodium and oxidation.

In particular, the composition prevents the deformation of cathode blocks caused by the attack of sodium or air, which in turn prevents the formation of dangerous nitrogen compounds such as cyanides. Cell efficiency is also improved, as the NaF present in the electrolyte used for aluminum production is no longer consumed by the reaction of NaF with the carbonaceous components of the cell. In this manner, the NaF concentration in the electrolyte bath can be precisely controlled without a need to replenish the bath with NaF.

It is another object of the present invention to provide a simple method for applying a protective composition to carbonaceous cell components of aluminum production cells, particularly cathode components such as sidewalls. The application method does not require reaction of the components in the composition in order to protect the component. The protective composition used in the present invention permits one to employ less expensive carbonaceous materials for the substrates into which the composition is impregnated. For example, cheaper grades of graphite, rather than the more expensive anthracite-based carbons or silicon carbides, may be employed for various cell components. The protective composition used in the present invention is inexpensive and also environmentally-safe.

The foregoing objects can be accomplished, in accordance with one aspect of the invention, by a method for treating a carbonaceous component of an electrolytic cell in order to prolong the useful life of the component, comprising the steps of applying a treatment composition to the component, wherein this treatment composition consists essentially of a non-colloidal solution of one or more phosphates of aluminum. The term "non-colloidal" simply means that the phosphates are dissolved in the solvent (i.e., a single-phase solution is formed). The phosphates of aluminum may be selected from the group consisting of: monoaluminum phosphate, aluminum phosphate, aluminum polyphosphate, aluminum metaphosphate, and mixtures thereof. Preferably, monoaluminum phosphate is employed in an aqueous solution.

The treatment composition used herein is effective in preventing oxidation of the sidewalls of an aluminum production cell, particularly when the phosphate concentration is between about 30 and about 60 weight percent of the total composition. Preferably, an aqueous solution of monoaluminum phosphate is employed, wherein the monoaluminum phosphate is present at a concentration of between about 30 and about 60 weight percent, most preferably between about 45 and 55 weight percent. In order to ensure that the monoaluminum phosphate does not hydrolyze, the ratio of  $P_2O_5$  to  $Al_2O_3$  is preferably greater than about 3. The treatment composition of the present invention should be applied to the sidewalls such that the phosphates will not contaminate the molten aluminum, by insuring that the treatment composition is only applied to the portions of the sidewalls which will not directly contact the molten aluminum or by applying another coating over the phosphates of aluminum, such as the coating described in PCT published application WO 93/25731. As is well known, during operation of a Hall-Héroult aluminum production cell, a solidified cryolite crust or a "ledge" is formed on the sides of the cell. The treatment composition is applied, *at least*, on the portion of the cell sidewall typically extending from the ledge to the topmost exposed portion of the sidewall.

The phosphates of aluminum used herein prevent oxidation of carbonaceous substrates and simultaneously prevent sodium intercalation. This is critical because a

carbonaceous portion which is contaminated with sodium is more susceptible to air oxidation than an uncontaminated portion.

If appropriate, the entire sidewall may be treated in accordance with the present invention, such as when a portion of the sidewall is susceptible to direct contact with the cryolite, for example during start-up or as a result of a prolonged anode effect. Even more preferably, in addition to coating the exposed surface of the sidewall, the outside portions (toward the shell of the cell) of the sidewall may also be treated. This provides added protection from air oxidation and also provides protection against sodium contamination of the outside portions due to fumes and Na ions from the cryolite, without danger of contaminating the molten cryolite/aluminum with phosphates.

Finally, the portions of the sidewall covered by the ledge may be treated in addition to the exposed portions. Contamination of molten cryolite by the phosphates of the treatment compositions used herein is avoided due to the solidified cryolite "ledge", as will be described in greater detail below. Optionally, for additional protection from contamination of the cryolite due to phosphates, the aluminum-wettable coating of WO 93/25731 may be applied on top of the treated sidewalls, particularly on any portion of the sidewall liable to be exposed to the molten cryolite.

The treatment composition used herein can be applied by dipping the component in the composition, painting the component with the composition, spraying the component with the composition, or pouring the composition onto the component. If spraying is chosen, the treatment composition is advantageously sprayed with steam. The component may then be dried after this application step, and this drying may be optionally followed by a heat treatment step. The entire process occurs at temperatures up to about 200°C. The composition may also be applied in several steps, wherein the treatment composition applied during each step is allowed to dry at least partially prior to the next application.

This same method may be employed using a treatment composition consisting essentially of a mixture of one or more non-colloidal phosphates of aluminum and one



or more colloidal carriers. The details regarding the colloidal carrier are disclosed, for example, in published international application WO 94/24069.

In one embodiment, the monoaluminum phosphate is present at a concentration of between about 30 and 60 weight percent of the treatment composition. Alternatively, the total amount of phosphate applied preferably corresponds to 0.01 to 0.1, preferably 0.01 to 0.02 weight percent of the weight of the component. Preferably, the component is a sidewall.

There is also provided a carbonaceous component of a cell used for the electrolytic production of aluminum from alumina dissolved in molten cryolite-based electrolyte, wherein the component is impregnated with a coating consisting essentially of one or more non-colloidal phosphates of aluminum, and one or more colloidal carriers as discussed above. The component may be treated by the methods described above, and preferably may be a sidewall of the cell.

#### DETAILED DESCRIPTION OF THE INVENTION

The applicant has found that the application of non-colloidal phosphates of aluminum to carbonaceous cell components of aluminum production cells, produces unexpected and beneficial results. The resulting impregnation protects the cell component from corrosive attack by liquids (sodium from the cryolite) and gases (oxygen from air) present in the production cells, thereby significantly extending the useful life of the cell component, particularly cell sidewalls. This prevents the deformation of the impregnated component caused by the attack of sodium or air, which in turn prevents the formation of dangerous nitrogen compounds such as cyanides.

Impregnation of cell components with the phosphates of aluminum of the present invention also permits one to employ less expensive carbonaceous materials for the substrates thus impregnated. For example, cheaper grades of graphite, rather than the more expensive anthracite-based carbons, may be employed for various cell components.

The compositions used for the impregnation are also inexpensive, readily available and environmentally safe in handling.

In its simplest embodiment, a solution consisting essentially of one or more non-colloidal phosphates of aluminum is prepared. The solution can, for example, be an aqueous, homogeneous, single-phase composition of one or more phosphates of aluminum. In particular, an aqueous solution of monoaluminum phosphate ( $\text{Al}(\text{H}_2\text{PO}_4)_3$ ) is prepared merely by dissolving the phosphate in water. The concentration of phosphate in the solution can be varied depending upon the component being treated, as well as the method of treatment (e.g., dipping versus multi-step spraying). In one presently preferred composition, particularly for treating cell components such as sidewalls, the sidewalls are treated so as to result in a concentration between about 0.01 to 0.1 preferably 0.01 and about 0.02 weight percent of phosphates of aluminum by weight of the sidewall, particularly when monoaluminum phosphate is employed. Varying concentrations of the treatment compositions may also be effectively employed, depending upon the degree of protection desired, as well as the type(s) and cost(s) of the phosphates of aluminum employed.

In addition to monoaluminum phosphate (also known as aluminum dihydrogenphosphate, aluminum orthophosphate, and acid aluminum phosphate), any other phosphate of aluminum may similarly be employed. These include: aluminum phosphate, aluminum polyphosphate, aluminum metaphosphate ( $\text{Al}(\text{PO}_3)_3$ ), and similar compounds. Thus, the present invention is not limited to the use of monoaluminum phosphate.

The present invention also embraces the use of a treatment composition consisting essentially of a solution of one or more non-colloidal phosphates of aluminum and one or more colloidal carriers. These colloids can be chosen from the group consisting of: alumina, silica, yttria, ceria, thoria, zirconia, magnesia, lithia, cerium acetate, and mixtures thereof. The compositions containing colloidal carriers can also be utilized for the same types of cell components described above. Details of the

colloidal carriers are described, for example, in published international application WO 94/24069.

The treatment composition may optionally also contain at least one compound selected from compounds of lithium, aluminum, cerium, sodium and potassium, for instance at least one compound of lithium and at least one compound of aluminum (see U.S. Patent No. 5,397,450, the contents of which are incorporated herein by way of reference).

Cell sidewalls are typically exposed to air and other oxidizing gases, and are therefore highly susceptible to degradation caused by oxidation. Oxidation is further increased due to the presence of sodium ions in the cell environment. To overcome this problem, the prior art has proposed replacing carbon sidewalls with much more expensive silicon carbide based sidewalls. In addition to the cost being prohibitive, silicon carbide bricks have also been known to inexplicably deteriorate at random under normal cell operating conditions. As an alternative to silicon carbide bricks, micropyrethically synthesized, pitch-free carbon sidewalls have also been developed (See, U.S. Patent No. 5,374,342). However these materials are also more expensive than conventional carbon sidewalls.

The treatment compositions described previously herein can be effectively employed for a number of different aluminum production cell components in particular cell sidewalls without a risk of contamination of the molten cryolite and/or aluminum. The conventional wisdom is that phosphates must be avoided because of the likely contamination of the product aluminum. See for example U.S. Patent No. 5,492,604, column 1. The applicant has surprisingly found, however, that phosphates of aluminum may be employed for the treatment of carbon sidewalls without a risk of product contamination, thereby greatly increasing the life of these sidewalls. This is counter indicated by the teaching away in the prior art from use of phosphates in aluminum production cells.

One particularly preferred composition for the treatment of cell sidewalls and/or cell bottoms consists essentially of between about 30 and about 60 weight percent monoaluminum phosphate in water, most preferably between about 45 and about 55 weight percent, wherein the monoaluminum phosphate is dissolved (i.e., non-colloidal). Monoaluminum phosphate is soluble in water, however it may hydrolyze to form the insoluble hydroxy phosphate if an acidic solution is not maintained. An acidic solution may be maintained by providing a slight excess of phosphoric acid in the solution in order to prevent hydrolyzation of the monoaluminum phosphate. The ratio of  $P_2O_5$  to  $Al_2O_3$  is therefore preferably at least about 3.0, more preferably greater than 3.0, and most preferably 3.05 to 3.1, in order to maintain such an acidic solution (pH less than about 3). Solutions of monoaluminum phosphate in water (typically approximately 50% by weight) are commercially available, or the solution may be prepared just prior to treatment of the sidewalls by any of a number of known methods.

The treatment compositions used in the present invention which include non-colloidal phosphates may additionally employ one or more of the non-phosphate colloidal carriers described previously. Thus, the present invention also comprises a treatment composition for cell sidewalls, wherein this composition consists essentially of a non-colloidal solution of one or more phosphates of aluminum (preferably between about 30 and about 60 weight percent), and one or more colloidal carriers (preferably between about 10 and about 20 weight percent). These colloids may be chosen from the group consisting of: alumina, silica, yttria, ceria, thoria, zirconia, magnesia, lithia, cerium acetate, and mixtures thereof.

#### **Methods of Application**

The treatment compositions of the present invention can be applied to cell components of aluminum production cells by any of a number of methods, including painting (by brush or roller), dipping (possibly assisted by a pressure differential), spraying (with steam or without), or pouring the composition onto the substrate. After drying, additional treatments may be applied in the same fashion. The treated component need not be entirely dry, however, before the application of the next treatment. Drying

may be carried out in ambient conditions, but optionally the treated component may be heated with a suitable heat source so as to completely dry it. Heating takes place preferably in air but could be in other oxidizing atmospheres, or in inert or reducing atmospheres. A heat treatment in air at about 80-200°C, for half an hour to several hours is usually sufficient, and heating beyond these temperatures is not needed.

The substrate being impregnated may also be treated by sand blasting or pickled with acids or fluxes such as cryolite or other combinations of fluorides and chlorides prior to the application of the compositions used herein. Similarly the substrate may be cleaned with an organic solvent such as acetone to remove oily residue and other debris prior to the application of the treatment composition.

After treatment according to the present invention, those parts of the impregnated substrate liable to be exposed to the molten cell content can be additionally impregnated with a slurry of pre-formed particulate refractory boride in a colloidal carrier, particularly where the colloidal carrier comprises at least one of colloidal alumina, silica, yttria, ceria, thoria, zirconia, magnesia, lithia, monoaluminum phosphate or cerium acetate. This slurry is the subject of published international application WO 93/25731. The use of the present invention in conjunction with this boride-containing slurry greatly enhances the effectiveness of the latter, particularly with regard to the aluminum-wettability of the carbonaceous surface.

The component being treated will usually be impregnated outside the aluminum production cell and then inserted into the cell. Alternatively, the component may be treated in place within the cell prior to operation. In such case, the treatment is "cured" *in-situ* by contact and hence heating, by the molten cell content. Also, carbonaceous cell sidewalls may be treated in several steps with drying of each successive treatment and final drying by means of a mobile heat source (e.g., 100-200°C for several minutes to about half an hour).

The treatment compositions used herein also permit the use of carbonaceous substrates of low-density carbon in some instances. Low density carbon embraces

various types of relatively inexpensive forms of carbon which are relatively porous and very conductive, but previously could not be used successfully in the environment of aluminum production cells on account of the fact that they were subject to excessive corrosion or oxidation. The present invention enables the use of these low density carbons, instead of the more expensive high density anthracite and graphite, taking advantage of their excellent conductivity and low cost.

Application of the treatment solution of the present invention (consisting essentially of, for example, 30 to 60 weight percent non-colloidal phosphates of aluminum) to cell sidewalls can be accomplished as described above, however the treatment composition is preferably applied to the sidewalls such that the phosphates will not contaminate the molten contents of the cell during cell operation. As mentioned above, and as will be described in greater detail below, heating of the cell during cell start-up leads to the formation of a frozen or solidified cryolite "ledge", which seals off portions of the sidewall from the molten cryolite and the oxidizing gases. In most cases, the presence of the ledge will insure that no portion of the sidewall contacts the molten cryolite, and thus the entire sidewall may be treated with the solutions of the present invention without contamination problems. Alternatively, only the portion of the sidewall extending above the molten aluminum pool may be treated. In this latter case, the treatment composition may possibly be applied *in situ*, thereby ensuring that only the portion of the sidewall extending above the molten aluminum is treated.

To further prevent contamination of the molten cryolite/aluminum when the treatment compositions of the present invention are employed at locations under the melt line, protective treatments may be applied over the phosphates of aluminum, particular in the region which would be liable to contact the molten cryolite/aluminum. For example, the treatment methods of U.S. Patent No. 5,378,327 (which is herein incorporated by reference) can be employed after application of the treatment compositions used herein for those portions of the sidewalls which are expected to contact the molten cryolite/aluminum. Alternatively, the refractory coating of U.S. Patent No. 5,310,476 may be applied after treatment with the solution of the present invention, particular on the regions of the sidewall which would be expected to contact

the molten cryolite/aluminum. Alternatively the slurry of published international application WO 93/25731 (MOL0521) may be applied after treatment with the solution of the present invention, particular on the regions of the sidewall which would be expected to contact the molten cryolite/aluminum.

### Example 1

In order to demonstrate the ability of one embodiment of the present invention to prevent oxidation and sodium related damage of cell sidewalls and cell bottoms, a non-colloidal solution of monoaluminum phosphate was applied to samples of carbon sidewalls. Specifically, 2x2x6 cm samples of a 70% anthracite/30% graphite sidewall material were dried at 150°C for approximately 24 hours to remove any moisture present. A non-colloidal, 50 weight percent monoaluminum phosphate aqueous solution (approx. 8%  $\text{Al}_2\text{O}_3$  and 34%  $\text{P}_2\text{O}_5$ ) was then placed into a container (the pH of a 1% solution is about 2.5). The solution volume was at least five times greater than the volume of the samples to be coated, and the container was shaped to ensure that the samples would be totally immersed. Samples to be coated were immersed in the monoaluminum phosphate solution at room temperature, and bubbling was observed at the surface of the sample. The samples were permitted to remain in the monoaluminum phosphate solution for 12 hours, and were then removed and excess solution wiped away. The samples were dried in a furnace at a temperature of 180° - 200° C for 24 hours. Thereafter, any powder remaining on the surface of the sample was wiped away.

In order to evaluate the ability of the treatment compositions of the present invention to provide increased sodium resistance, an accelerated sodium penetration test was employed. Samples treated in the just-described manner were employed, along with untreated samples. The test consisted of cathodically polarizing the samples in an approximately 33/67 weight percent sodium fluoride/sodium chloride electrolyte at about 710°C and at a current density of between 0.15 and 0.1 A/cm<sup>2</sup>. These test conditions simulate the effects of sodium penetration under normal working conditions over much longer periods. After just 1.5 hours, the untreated samples had totally disintegrated. The treated samples, on the other hand, exhibited no visible change even after 4 hours. Thus,

surprisingly, the compositions of the present invention are effective in preventing sodium damage of cell sidewalls.

In order to determine the effectiveness of the treatment composition of the present invention for preventing air oxidation of cell sidewalls, the oxidation resistance of these treated samples was compared with that of untreated samples. The test employed comprised heating each sample to the specified temperature in air, and periodically measuring the weight of the sample in order to determine the rate of oxidation. The untreated samples exhibited an oxidation rate (measured in terms of weight loss) of  $0.0225 \text{ g/cm}^2 \text{ hr}$  at  $500^\circ\text{C}$ , and disintegrated into a powdery material after only about 8 hours. When oxidation tests were performed on untreated samples at even higher temperatures (up to  $800^\circ\text{C}$ ), the untreated samples quickly disintegrated. In contrast, samples treated using the composition of the present invention in the manner described above performed remarkably well. At  $500^\circ\text{C}$ , little oxidation was observed during the first 6 hours, and oxidation reached a maximum rate of only  $0.0064 \text{ g/cm}^2 \text{ hr}$ . At  $600^\circ\text{C}$ , the rate of oxidation increased to only  $0.019 \text{ g/cm}^2 \text{ hr}$ . At  $700^\circ\text{C}$  the rate of oxidation was  $0.030 \text{ g/cm}^2 \text{ hr}$ , and at  $800^\circ\text{C}$  it was  $0.04 \text{ g/cm}^2 \text{ hr}$ . Thus, it is seen that the compositions of the present invention are effective in preventing oxidation of cell sidewalls, even at elevated temperatures. While not wanting to be bound by any particular theory, it is believed that the treatment methods of the present invention prevent oxidation of the carbonaceous substrate by protecting the binder phase of the carbonaceous substrate from oxidation.

### Example 2

As an alternative to the immersion technique described above, it is possible to impregnate the solution of Example 1 by spraying with steam. One advantage of the steam process is that an *installed* sidewall may be treated with the treatment composition of Example 1 instead of treatment *prior* to installation. A steam applicator is initially flushed with the treatment composition of Example 1. When the steam applicator is ready the steam-phosphate solution is directed on the sidewall preferably for at least 5 minutes. The sample is then dried as described above. Multiple step application as



described above is also possible. Oxidation resistance of the sidewalls treated by this method has been observed to be comparable to that obtained by the method of Example 1.

It will be understood that modifications may be made in the present invention without departing from the spirit of it. Thus, the scope of the present invention should be considered in terms of the following claims, and is understood not to be limited to the details of operation described in the specification.

**CLAIMS**

1. A method for treating a carbonaceous component, in particular a sidewall of an electrolytic aluminum production cell in order to prolong the useful life of said component, comprising the step of applying a treatment composition to said component, said treatment composition consisting essentially of a non-colloidal solution of one or more phosphates of aluminum.
2. The method of claim 1, wherein said phosphates of aluminum are selected from the group consisting of: monoaluminum phosphate, aluminum phosphate, aluminum polyphosphate, aluminum metaphosphate, and mixtures thereof.
3. The method of claim 2, wherein said phosphates are present at a concentration of between about 30 and about 60 weight percent by total weight of said solution.
4. The method of claim 3, wherein said phosphates are present at a concentration of between about 45 and about 55 weight percent by total weight of said solution.
5. The method of claim 4, wherein said phosphate is monoaluminum phosphate.
6. The method of claim 5, wherein the ratio of  $P_2O_5$  to  $Al_2O_3$  is greater than about 3.
7. The method of claim 1, further comprising the step of drying said component after said application step.
8. The method of claim 7, wherein said application step is accomplished by dipping said component in said composition, painting said component with said

composition, spraying said component with said composition, or pouring the composition onto said component.

9. The method of claim 8, wherein said spraying is carried out together with steam.

10. The method of claim 1, wherein said method is carried out at temperatures up to about 200°C.

11. The method of claim 7, wherein said drying is followed by a heat treatment step.

12. The method of claim 11, wherein said heat treatment is carried out at temperatures up to about 200°C.

13. The method of claim 7, wherein said composition is applied in multiple steps, and wherein the composition is allowed to dry at least partially prior to the next step.

14. The method of claim 1, further comprising treatment by at least one compound selected from compounds of lithium, aluminum, cerium, sodium and potassium.

15. The method of claim 1, further comprising treatment by at least one compound of lithium and at least one compound of aluminum.

16. A component of a cell used for the electrolytic production of aluminum from alumina dissolved in molten cryolite electrolyte, in particular a cell sidewall, wherein said component is impregnated with a treatment solution consisting essentially of a non-colloidal solution of one or more phosphates of aluminum.

17. The component of claim 16, wherein said phosphates of aluminum are selected from the group consisting of: monoaluminum phosphate, aluminum phosphate, aluminum polyphosphate, aluminum metaphosphate, and mixtures thereof.

18. The component of claim 17, wherein said phosphates are present at a concentration of between about 30 and about 60 weight percent by total weight of said solution.

19. The component of claim 18, wherein said phosphates are present at a concentration of between about 45 and about 55 weight percent by total weight of said solution.

20. The component of claim 19, wherein said phosphate is monoaluminum phosphate.

21. The component of claim 20, wherein the ratio of  $P_2O_5$  to  $Al_2O_3$  is greater than about 3.

22. The component of claim 16, further comprising treatment by at least one compound selected from compounds of lithium, aluminum, cerium, sodium and potassium.

23. The component of claim 16, further comprising treatment by at least one compound of lithium and at least one compound of aluminum.

24. The component of claim 16, wherein said phosphates of aluminum are present at a level ranging from 0.01 to 0.1, preferably from 0.01 to 0.02 weight percent by total weight of said component.

25. A method for treating a carbonaceous electrolytic cell component in order to prolong the useful life of said component, comprising the step of applying a treatment composition to said component, said treatment composition consisting essentially of a

5 solution of one or more non-colloidal phosphates of aluminum and one or more colloidal carriers.

26. The method of claim 25, wherein said colloidal carrier is chosen from the group consisting of: colloidal alumina, silica, yttria, ceria, thoria, zirconia, magnesia, lithia, cerium acetate, and mixtures thereof

27. The method of claim 26, wherein the composition has a dry colloid content of up to about 50 weight percent of said composition.

28. The method of claim 25, wherein said method is carried out at temperatures up to about 200°C.

29. The method of claim 25, further comprising the step of drying said component after said application step.

30. The method of claim 29, wherein said drying is followed by a heat treatment step.

31. The method of claim 25, wherein said composition is applied in multiple steps, and wherein the composition is allowed to dry at least partially prior to the next step.

32. The method of claim 25, wherein said phosphate is monoaluminum phosphate.

33. The method of claim 32, wherein said monoaluminum phosphate is present in said component at a concentration of between about 0.01 and about 0.02 weight percent by total weight of said component.

34. The method of claim 33, wherein said monoaluminum phosphate is present at a concentration of between about 30 and about 60 weight percent in said treatment composition.

35. The method of claim 32, further comprising treatment by at least one compound selected from compounds of lithium, aluminum, cerium, sodium and potassium.

36. The method of claim 32, further comprising treatment by at least one compound of lithium and at least one compound of aluminum.

37. A carbonaceous component of a cell used for the electrolytic production of aluminum from alumina dissolved in molten cryolite electrolyte, wherein said component is impregnated with a coating consisting essentially of one or more non-colloidal phosphates of aluminum, and one or more colloidal carriers.

38. The component of claim 37, wherein said impregnation is carried out at a temperature of up to about 200°C.

39. The component of claim 38, wherein said phosphates of aluminum are selected from the group consisting of: monoaluminum phosphate, aluminum phosphate, aluminum polyphosphate, aluminum metaphosphate, and mixtures thereof.

40. The component of claim 39, wherein said colloidal carrier is chosen from the group consisting of: colloidal alumina, silica, yttria, ceria, thoria, zirconia, magnesia, lithia, cerium acetate, and mixtures thereof.

41. The component of claim 40, wherein said phosphate is monoaluminum phosphate.

42. The component of claim 41, wherein said component is a sidewall of said cell.

43. The component of claim 42, wherein said monoaluminum phosphate is present in said sidewall at a concentration of between about 0.01 and about 0.02 weight percent of said sidewall.

44. The component of claim 43, wherein said component is a cathode block of said cell.

45. The component of claim 43, wherein said component is the cell bottom of said cell.

46. An electrolytic cell for the production of aluminum including the component of claim 1 or claim 37, wherein said component is shielded from the molten cryolite by a solidified cryolite crust.

47. The cell of claim 46, wherein the component is a sidewall.

# INTERNATIONAL SEARCH REPORT

Int. l. application No.  
PCT/US96/11385

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B05D1/02, 1/18, 3/02; B32B 9/00; C25B 11/00, 11/12; C25D 3/56.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/243R, 279, 280, 290R, 294; 205/159, 230, 318; 427/372.2, 377, 379, 380, 397.7, 421, 422, 430.11, 443.1; 428/408.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: phosphat?, carbon?, coat?, aluminum.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5,364,513 (SEKHAR ET AL) 15 November 1994.	
A	US, A, 5,254,232 (SADOWAY) 19 October 1993	

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A		document defining the general state of the art which is not considered to be of particular relevance
* E		earlier document published on or after the international filing date
* L		document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
* O		document referring to an oral disclosure, use, exhibition or other means
* P		document published prior to the international filing date but later than the priority date claimed
	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
	* &	document member of the same patent family

Date of the actual completion of the international search

03 SEPTEMBER 1996

Date of mailing of the international search report

27 DEC 1996

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# INTERNATIONAL SEARCH REPORT

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PCT/US96/11385

**A. CLASSIFICATION OF SUBJECT MATTER:**  
**US CL :**

204/179, 243R, 290R, 294; 205/159, 230, 318; 427/372.2, 377, 379, 380, 397.7, 421, 422, 430.11, 443.1; 428/408.